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(54) **Lubricating oils**

(57) Lubricating oils for use as engine oils comprise from 30 to 95% by weight of an ester of a hindered alcohol and an unsaturated fatty acid containing 18 carbon atoms, and from 70 to 5% by weight of a mineral oil and/or a synthetic oil.

SPECIFICATION

Lubricating oils

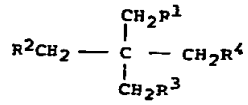
The invention relates to lubricating oils.

Various synthetic lubricating oils are known as lubricants for use at high temperature. Their upper temperature limits, however, are between 170 and 200°C. If they are used at temperatures above 200°C, various problems arise; for example, evaporation of the lubricating oil leading to loss of lubrication, or the lubricating action of the lubricant is reduced or lost by the formation of sludge. Hence the conventional synthetic lubricating oils are not suitable for use at such high temperatures.

Lubricants for use in an engine of adiabatic type, a super high temperature gas turbine bearing, turbocharged engines and so forth are required to withstand temperatures as high as 200°C or more, particularly temperatures as high as 300°C or more. Major characteristics required for lubricants being used at such high temperatures are (1) the evaporation loss at high temperatures is small; (2) sludge is not formed at high temperatures; (3) stability against oxidation is good; and (4) load-carrying capacity is high.

The invention provides a lubricating oil comprising from 30 to 95% by weight of an ester of a hindered alcohol and an unsaturated fatty acid containing 18 carbon atoms and from 70 to 5% by weight of a mineral oil and/or a synthetic oil.

Various hindered alcohols can be used to form the ester, including those compounds represented by the general formula



wherein each of R^1 to R^4 independently represents a hydrogen atom, a hydroxy group, a hydroxyalkyl group or an alkyl group, provided that at least one of R^1 to R^4 represents a hydroxy group or a hydroxyalkyl group. The hydroxyalkyl and alkyl groups preferably contain from 1 to 3 carbon atoms. Preferred hindered alcohols are 2,2-di-(hydroxymethyl)-butanol, 2,2,-di(hydroxymethyl)-propanol, pentaerythritol, 2-methyl-2-hydroxymethyl-propanol and 2-methyl-2-hydroxymethyl-pentanol. Alternatively, the hindered alcohol may be a compound such as dipentaerythritol.

Suitable unsaturated fatty acids include oleic acid, linoleic acid and linolenic acid. These acids may be used as their derivatives (e.g., acid halides).

Examples of suitable esters include 2,2-di(oleoyloxymethyl)-butyl oleate, pentaerythritol tetraoleate, dipentaerythritol hexaoleate, 2-methyl-2-oleoyl-oxymethyl-propyl oleate, 2,2-di(linoleoyloxymethyl)-butyl linoleate, pentaerythritol tetralinolate, dipentaerythritol hexalinolate, 2-methyl-2-linoleoxymethyl-propyl oleate, 2,2-di(linolenoyloxymethyl)-butyl linolenate, pentaerythritol tetralinolenate, dipentaerythritol hexalinolenate and 2-methyl-2-linolenoyloxymethyl-propyl linolenate.

The mineral oil and the synthetic oil may be used singly or in combination with each other. Various types of mineral oils, such as naphthenic and paraffinic mineral oils, can be used. In general, those mineral oils which are known as lubricating base oils can be used. Also, various types of synthetic oils can be used. Examples of such synthetic oils include α-olefin polymers having a degree of polymerization of about from 20 to 200, such as ethylene homopolymers, propylene homopolymers, butene homopolymers and ethylene propylene copolymers; organic phosphates, such as alkyl phosphates and aryl phosphates; organic silicates, such as alkyl silicates and aryl silicates and carboxylates. These carboxylates include esters obtained by reacting dibasic acids such as adipic adic, azelaic acid and sebacic acid, or straight or branched chain saturated fatty acids containing from 5 to 30 carbon atoms, with 2-ethylhexanol, *s*-butanol, 3-methylbutanol or hindered alcohols.

The viscosity of the mineral oil or synthetic oil is not critical. In general, it is preferred to use a mineral oil or a synthetic oil having a kinematic viscosity at 100°C of at least 5 centistokes, especially from 10 to 50 centistokes.

The lubricating oil of the invention preferably contains from 50 to 90% by weight of the ester and from 50 to 10% by weight of the mineral oil and/or synthetic oil. If the proportion of the ester is too small, the lubricating oil is not stable at high temperature, whereas if it is too large, the oxidation stability drops.

The lubricating oil according to the invention may, if necessary, further comprise various additives such as amine-, phenol-, and dithiophosphoric acid-type antioxidants, sulphonate-, phenete-, phosphonate-, and salicylate-type detergent dispersants, sulphur/phosphorus-, and phosphate-type extreme pressure agents, and oiliness agents.

Even if the lubricating oil of the invention is used at temperatures as high as 200°C or more, particularly about 300°C, its evaporation loss is small and little sludge is formed. Furthermore the lubricating oil of the invention has a high oxidation stability and a high load-carrying capacity.

Hence the lubricating oil of the invention is suitable for the lubrication of machine elements subjected to high temperatures of 200°C or more, particularly in internal combustion engines; that is, is suitable for use as an engine oil.

The invention is illustrated by the following Examples.

Examples 1 to 13

Lubricating oil compositions having the formulations described in the Table were prepared, and their physical properties were measured by the following tests.

The following physical properties were tested.

Test of Thermal Stability:

A lubricating oil sample (30 grams) was placed in a beaker as specified in Figure 153 of JIS K2839 and maintained at 320°C for 3 hours. At the end of the time, the evaporation loss and the formation of

sludge were determined.

Indiana stirring oxidation test: measured according to JIS K2514.

Falex friction test of Load-Carrying Capacity: measured according to ASTM D3233.

The results are shown in the Table.

TABLE

	EXAMPLE								
	1	2	3	4	5	6	7	8	9
Lubricating Oil Composition (parts by weight)									
Ester of 2,2-di (hydroxymethyl)-butanol and oleic acid*1	30	50	70	70	90	95	70	50	
Ester of pentaerythritol and oleic acid*2									50
Ester of pentaerythritol and linolic acid*3									
Paraffinic mineral oil*4				30				50	
α-olefin homopolymer*5							15		50
Saturated hindered ester *6	70	50	30		10	5	15		
Phenothiazine	1	1	1	1			1		1
Dioctyldiphenylamine					1				
α-Naphthylamine						1			
Calcium sulphonate (TBN 25)	5	5	5		5	5			5
Calcium phenate (TBN 150)	5	5	5		5	5			5
Calcium salicylate (TBN 170)				5					
Tricresyl phosphate							1		
Physical Properties									
Test of Thermal Stability									
Evaporation loss (% by weight)	25	21	19	20	17	15	20	28	27
Formation of sludge	None	None	None	None	None	None	None	None	None
Indiana stirring oxidation test									
Increase in viscosity (viscosity ratio) as determined at 40°C	1.3	1.5	2.1	2.3	2.5	2.5	2.3	2.0	1.5
Total acid value	2.5	2.9	4.9	5.0	7.6	8.0	5.6	3.0	3.1
Falex friction test of load-carrying Capacity (LBS)	1100	1100	1100	1100	1100	1100	1300	110	1000

Table (Continued)

	Example			
	10	11	12	13
Lubricating Oil Composition (parts by weight)				
Ester of 2,2-di(hydroxymethyl)--butanol and oleic acid*1				
Ester of pentaerythritol and oleic acid*2	70	90	50	
Ester of pentaerythritol and linolic acid*3				30
Paraffinic mineral oil*4		10		
α-Olefin homopolymer*5	30			
Saturated hindered ester*6			50	70
Phenothiazine	1			1
Dioctyldiphenylamine		1		
α-Naphthylamine				
Calcium sulphonate (TBN=25)		5		5
Calcium phenate (TBN=150)		5		5
Calcium salicylate (TBN=170)	5			
Tricresyl phosphate				
Physical Properties				
Test of Thermal Stability				
Evaporation loss (% by weight)	22	16	29	21
Formation of sludge	None	None	None	None
Indiana stirring oxidation test				
Increase in viscosity (viscosity ratio) as determined at 40°C	2.4	2.5	1.9	1.7
Total acid value	5.3	7.9	3.8	8.0
Falex friction test of Load-Carrying Capacity (LBS)	1100	1200	1100	1100

Note:

*1 Unister H-381R, produced by Nippon Oils & Fats Co., Ltd.

*2 Unister H-481R, produced by Nippon Oils & Fats Co., Ltd.

*3 Prepared by the esterification of pentaerythritol and linolic acid.

*4 Viscosity at 100°C: 30 centistokes

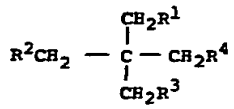
*5 Lucant HC, produced by Mitsui Petrochemical Co. Ltd. (an ethylene-propylene copolymer; viscosity (100°C): 20 centistokes)

*6 Composite ester of 2,2-di(hydroxymethyl)-butanol, adipic acid, and stearic acid (Unister C-3373H, produced by Nippon Oils & Fats Co., Ltd.)

CLAIMS

1. A lubricating oil comprising from 30 to 95% by weight of an ester of a hindered alcohol and an unsaturated fatty acid containing 18 carbon atoms and from 70 to 5% by weight of a mineral oil and/or a synthetic oil.

2. A lubricating oil according to claim 1 in which the hindered alcohol has the general formula



wherein each of R^1 to R^4 independently represents a hydrogen atom, a hydroxy group, a hydroxyalkyl group or an alkyl group, provided that at least one of R^1 to R^4 represents a hydroxy group or a hydroxyalkyl group.

3. A lubricating oil according to claim 1 or claim 2 in which the hindered alcohol is 2,2-di(hydroxymethyl)-butanol, 2,2-di(hydroxymethyl)-propanol, pentaerythritol, 2-methyl-2-hydroxymethyl-propanol or 2-methyl-2-hydroxymethyl-pentanol.

4. A lubricating oil according to any preceding claim in which the unsaturated fatty acid is oleic acid, linoleic acid or linolenic acid.

5. A lubricating oil according to claim 1 or claim 2 in which the ester is 2,2-di(oleoyloxy-methyl)-butyl oleate, pentaerythritol tetraloeate, dipentaerythritol hexaoleate, 2-methyl-2-oleoyloxy-methyl-propyl oleate, 2,2-di(linoleoyloxymethyl)-butyl linoleate, pentaerythritol tetralinolate, dipentaerythritol hexalinolate, 2-methyl-2-linoleoyloxymethyl-propyl oleate, 2,2-di(linolenoyl-oxymethyl)-butyl linolenate, pentaerythritol tetralinolenate, dipentaerythritol hexalinolenate or 2-methyl-2-linolenoyloxymethyl-propyl linolenate trimethylolpropane trioleate, pentaerythritol tetraoleate, dipentaerythritol hexaloeate, neopentyl glycol dioleate, trimethylolpropane trilinolate, pentaerythritol tetralinolate, dipentaerythritol hexalinolate, neopentyl glycol dilinolate, trimethylolpropane trilinolenate, pentaerythritol tetralinolenate, dipentaerythritol hexalinolenate or neopentyl glycol dilinolenate.

6. A lubricating oil according to any preceding claim in which the mineral oil is a naphthenic mineral oil or a paraffinic mineral oil.

7. A lubricating oil according to any of claims 1 to 5 in which the synthetic oil is an α-olefin polymer having a degree of polymerization of from 20 to 200, an organic phosphate, an organic silicate or a carboxylate.

8. A lubricating oil substantially as described herein with reference to any of the Examples.

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